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(54) Cyanide-free copper plating bath

(57) An electroless or electrolytic plating bath contains 5–70g/l. copper salt eg sulphate, 20–200g/l. tetrapotassium pyrophosphate, 2–20g/l. boric acid, and 2.5–60ml./l. of an aq. additive comprising i) 1–90ml./gal. acetaldehyde, ii) 10–200ml./gal. formaldehyde, iii) 1–90 ml./gal. alcohol eg n–propyl alcohol and iv) 1–90 ml./gal. surfactant. The deposits are fine-grained.

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CYANIDE-FREE COPPER PLATING BATH AND PROCESS

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

This invention relates to the field of copper plating, and particularly to an aqueous cyanide-free plating bath and process for the electrodeposition or electroless plating of copper.

BACKGROUND ART

The most common industrial process for electrodeposition of copper employs a plating bath containing cyanide salts. This process has numerous disadvantages, the most significant of which is the toxicity of the cyanide electrolyte and the environmental hazards attendant to its use and disposal. Because of these hazards, a variety of cyanide-free electroplating processes have been proposed. For example, cyanide-free copper electrolytes and processes are disclosed in U.S. Patent Nos. 4,521,282 and 4,469,569.

The present invention provides a particularly advantageous copper plating process by providing an aqueous plating bath that is cyanide-free and which yields an extremely fine grained copper deposit.

SUMMARY OF THE INVENTION

The present invention provides an aqueous cyanide-free copper plating bath, which in the preferred embodiment contains copper sulfate, tetrapotassium pyrophosphate, boric acid and an aqueous additive, which in turn contains acetaldehyde, formaldehyde, an alcohol such as n-propyl alcohol and a surfactant.

The plating bath is mixed from commercially available chemicals that are low in toxicity, particularly when compared with a conventional cyanide plating bath. The process deposits fine grained, semi-bright copper at room temperatures on ferrous and non-ferrous substrates, including some aluminum alloys, and is highly tolerant of typical plating contaminants, particularly zinc.

DETAILED DESCRIPTION OF THE INVENTION

In the following description, for purposes of explanation and not limitation, specific substances, concentrations, etc. are set forth in order to provide a thorough understanding of the present invention. However, it will be apparent to one skilled in the art that the present invention may be practiced in other embodiments that depart from these specific details. In other instances, detailed descriptions of well known processes are omitted so as to not obscure the description of the present invention with unnecessary detail.

The preferred plating bath contains (1) copper sulfate as a source of copper ions, (2) tetrapotassium pyrophosphate (TKPP) as a crossover medium to facilitate migration of the copper ions, (3) boric acid to prevent polarization and oxidation of the anodes and (4) an aqueous additive to achieve a fine grain deposition of copper on the cathode surface.

The relative concentrations of the constituent chemicals are set forth in Table 1 below, the balance of the bath comprising deionized water. Minimum, nominal and maximum values are given for the concentrations of each constituent. The nominal values are known to provide satisfactory performance, and it is believed that comparable performance may be achieved with concentrations anywhere within the indicated ranges or even beyond. Thus, this invention is not strictly limited to the values given. Although copper sulfate is the preferred source of copper ions, certain

other copper salts may be found to be suitable substitutes within the scope of this invention. Likewise, appropriate substitutes for boric acid will be obvious to those skilled in the art.

TABLE 1

CONSTITUENT	CONCENTRATION		
	MINIMUM	NOMINAL	MAXIMUM
copper sulfate $CuSO_4$	5 g/l	30 g/l	70 g/l
TKPP	20 g/l	100 g/l	200 g/l
boric acid H_3BO_3	2 g/l	5 g/l	20 g/l
aqueous additive	2.5 ml/l	25 ml/l	60 ml/l

The plating bath is mixed according to the following procedure. An appropriate container is first filled to approximately 80% of the working volume with deionized water. The premeasured quantity of TKPP is then added while stirring continuously. Following complete mixing of the water and TKPP, the premeasured quantity of copper sulfate is added, while again stirring continuously. After complete mixing, the premeasured quantity of boric acid is added while still stirring the mixture continuously. Again, following complete mixing, the premeasured quantity of the aqueous additive described below is added and stirring is continued until complete mixing is achieved. Finally, the container is topped-off to its operating volume with deionized

water. The entire mixing process may be performed at room temperature.

The aqueous additive referred to above is mixed from the constituents listed in Table 2 below in the indicated concentrations per gallon of additive. As in Table 1, minimum, nominal and maximum concentrations are presented, but these are intended only as guidelines. The alcohol in the aqueous additive serves as a primary brightener, in the same fashion that ammonia is widely used in conventional processes. The alcohol is a primary contributor to this invention's resistance to zinc contamination. Most any common alcohol may be used, although n-propyl alcohol is preferred for economic reasons.

T A B L E 2

CONSTITUENT	CONCENTRATION (per gallon)		
	MINIMUM	NOMINAL	MAXIMUM
acetaldehyde CH_3CHO	1 ml	30 ml	90 ml
formaldehyde HCHO	10 ml	80 ml	200 ml
n-propyl alcohol $CH_3CH_2CH_2OH$	1 ml	30 ml	90 ml
"Triton X-100"	1 ml	30 ml	90 ml

"Triton X-100" is a trademark of Rohm & Haas Company designating a surfactant based on alkylaryl polyether alcohols,

sulfonates and sulfates. Use of this or a comparable surfactant is important for reducing stress in the plated surface, thereby enhancing the ductility of the plated copper.

The aqueous additive is preferably mixed by filling an appropriate container with deionized water to 75% of the final volume (i.e., approximately three quarts). The constituent chemicals are then added in the same sequence as listed in Table 2 while stirring continuously. The container is then topped-off with deionized water and the additive may be stored pre-mixed for use in the above-described plating bath.

The plating bath of the present invention is preferably maintained at a pH in the range of approximately 6-11 depending on the substrate to be plated. For ferrous substrates, a more acidic bath is preferred, whereas an alkaline bath is preferred for zinc. The bath does not exhibit temperature sensitivity and may be operated anywhere in the range of approximately 40° F to approximately 100° F. This is in distinct contrast to conventional copper plating baths which are generally operated at temperatures of approximately 125° F.

Plating may be performed as an electroless process or by electrodeposition in conventional rack, barrel or reel-to-reel equipment. The present invention requires only about two-thirds of the plating current of conventional processes. Typically, the plating current will be maintained in the range of approximately 5-30 ASF for immersion plating, whereas currents of 100 ASF or

higher may be utilized for high speed reel-to-reel processes. Moreover, plating proceeds at a faster rate than conventional processes, approximately twice as fast as a conventional cyanide process and approximately three times as fast as a conventional alkaline process. For plating currents in the range of 10-20 ASF, deposition rates of approximately 0.2-0.5 mil/minute are achieved.

It will be recognized that the above described invention may be embodied in other specific forms without departing from the spirit or essential characteristics of the disclosure. Thus it is understood that the invention is not to be limited by the foregoing illustrative examples except as set forth in the claims.

CLAIMS

1. An aqueous cyanide-free copper plating bath comprising:

(a) approximately 5-70 g/l copper salt free of cyanide;

(b) approximately 20-200 g/l tetrapotassium pyrophosphate;

(c) approximately 2-20 g/l boric acid;

(d) approximately 2.5-60 ml/l of an aqueous additive comprising:

(i) approximately 1-90 ml/gal acetaldehyde;

(ii) approximately 10-200 ml/gal aldehyde;

(iii) approximately 1-90 ml/gal alcohol;

(iv) approximately 1-90 ml/gal of a surfactant.

2. The bath of claim 1 wherein said copper salt is copper sulfate.

3. The bath of claim 1 wherein said aldehyde is formaldehyde.

4. The bath of claim 1 wherein said alcohol is n-propyl alcohol.

5. An aqueous cyanide-free copper plating bath comprising:

(a) approximately 5-70 g/l copper sulfate;

(b) approximately 20-200 g/l tetrapotassium pyrophosphate;

(c) approximately 2-20 g/l boric acid;

(d) approximately 2.5-60 ml/l of an aqueous additive comprising:

(i) approximately 1-90 ml/gal acetaldehyde;

(ii) approximately 10-200 ml/gal formaldehyde;

(iii) approximately 1-90 ml/gal alcohol;

(iv) approximately 1-90 ml/gal of a surfactant.

6. The bath of claim 5 wherein said alcohol is n-propyl alcohol.

7. An aqueous cyanide-free copper plating bath comprising:

(a) approximately 30 g/l copper sulfate;

(b) approximately 100 g/l tetrapotassium pyrophosphate;

(c) approximately 5 g/l boric acid;

(d) approximately 25 ml/l of an aqueous additive comprising:

(i) approximately 30 ml/gal acetaldehyde;

(ii) approximately 80 ml/gal formaldehyde;

(iii) approximately 30 ml/gal alcohol;

(iv) approximately 30 ml/gal of a surfactant.

8. The bath of claim 7 wherein said alcohol is n-propyl alcohol.

9. An aqueous cyanide-free copper plating bath substantially as hereinbefore described.

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Examiner's report to the Comptroller under Section 17 (The Search Report)

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Relevant Technical fields

(i) UK Cl (Edition) Contd. from page 1

(ii) Int Cl (Edition)

Databases (see over)

(i) UK Patent Office

(ii)

Search Examiner
M J INGLEY

Date of Search

Documents considered relevant following a search in respect of claims

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
Y	SU 1516512 (KAZAN KIROV) see Derwent Abstract No 90-237185/31	1,5,7 at least

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

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